Cooling of gases [tln23]

During expansion, a gas does work against attractive intermolecular forces. In the process, the average potential energy increases and, by virtue of energy conservation, the average kinetic energy decreases. The result is a drop in temperature. We discuss two processes to illustrate this effect.

Joule effect: free expansion

Free expansion involves no heat transfer and no work performance:
$\Delta Q = 0,\ \Delta U = 0,.$

Initial state: V_i, p_i, T_i; final state: V_f, p_f, T_f with $p_f < p_i$.

The temperature change in the expanding gas is calculated for a quasi-static process between the same equilibrium states.

Use $\left(\frac{\partial U}{\partial T}\right)_V = C_V, \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p$

Joule coefficient: $\left(\frac{\partial T}{\partial V}\right)_U = -\frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V} = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right].$

Ideal gas: $T\left(\frac{\partial p}{\partial T}\right)_V = p \ \Rightarrow$ no effect.

Joule-Thomson effect: throttling

The gas is forced through a porous wall between two chambers. During the process the pressure is constant in both chambers. In the following we consider quasi-static throttling.

Initial state: V_i, p_i, T_i; final state: V_f, p_f, T_f with $p_f < p_i$.

$\Delta Q = 0,\ \Delta U = \Delta W = -\int_0^{V_f} p_f dV - \int_{V_i}^0 p_i dV = -p_f V_f + p_i V_i.$

$\Rightarrow\ U_i + p_i V_i = U_f + p_f V_f = \text{const.} \ \Rightarrow\ E = \text{const.} \ \Rightarrow\ dE = TdS + Vdp = 0.$

Use $\left(\frac{\partial E}{\partial T}\right)_p = C_p, \quad \left(\frac{\partial E}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = -T\left(\frac{\partial V}{\partial T}\right)_p + V.$

Joule-Thomson coefficient: $\left(\frac{\partial T}{\partial p}\right)_E = -\frac{(\partial E/\partial p)_T}{(\partial E/\partial T)_p} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right].$

Ideal gas: $T\left(\frac{\partial V}{\partial T}\right)_V = V \ \Rightarrow$ no effect.